OTS: 60-11,410

JPRS: 2394

28 March 1960

METHODS AND TECHNIQUE OF PHYSICO-CHEMICAL RESEARCH

- USSR -

by Ya. M. Varshavskiy and M.G. Lezhnina

Distributed by:

OFFICE OF TECHNICAL SERVICES
U. S. DEPARTMENT OF COMMERCE
WASHINGTON 25, D. C.

Price: $0.50

U. S. JOINT PUBLICATIONS RESEARCH SERVICE
205 EAST 42nd STREET, SUITE 300
NEW YORK 17, N. Y.

JPRS: 2394

CSO : 3575-N

METHODS AND TECHNIQUE OF PHYSICO-CHEMICAL RESEARCH

A Method for Investigating the Hydrogen Isotope Exchange in a Liquid Deuterium Floride Medium

[This is a translation of an article written by Ya. M. Varshavskiy and M. G. Lozhnina, in Zhurnal Fizicheskoy Khimii (Journal of Physical Chemistry), Vol XXXI, No 4, 1957, pages 911-914]

To compare the reactivities of organic compounds during electrophilic hydrogen exchange reactions, and also to study the effect of the dielectric constant of the solvent on the rate of hydrogen exchange in acid media, experiments were conducted for investigating the hydrogen exchange between various organic substances and liquid deuterium floride, catolyzed by boron trifluoride (see [1] and also the following papers).

A method for obtaining DF, described in [2], which consists in reducing AgF by gaseous deuterium at high temperature, proved to be inadequate for producing large quantities of DF. The method, used in our first experiment [1] to obtain large quantities of hydrogen fluoride enriched with deuterium, consisting of the addition of heavy water to hydrogen fluoride and its subsequent removal by electrolysis had a defect that caused the contamination of deuterium fluoride by fluorine oxide; a powerful oxidizing agent.

In the present paper methods are described for the generation of large quantities of hydrogen fluoride enriched with deuterium,* the analysis of its isotopes, and also the apparatus for the preparation of solutions in liquid DF and methods for conducting tests on the isotope exchange in this medium.

*Henceforth designated deuterium fluoride, DF.

The general appearance of the apparatus is illustrated in Fig 1. All parts which were subjected to the action of DF (including the valves) were made of monel metal and fluoroplastics, with the exception vessel 16 for the reception of DF, which is of copper. A part of the apparatus intended for the storage and dosage of BF_3 was made of glass. Linings and gaskets were prepared from toflon.

Deuterium fluoride was obtained by the thermal decomposition of previously deuterized potassium fluoride, KF•DF. The corresponding method for obtaining hydrogen fluoride which did not contain deuterium is described in reference [3]. Recrystallized and desiccated potassium bifluoride was dissolved in heavy water, the latter was distilled off and the "heavy" salt was subjected to preliminary drying at 110-120° C. Salt purification, isotope exchange and salt desiccation were conducted in a copper apparatus.

The "heavy" bifluoride was placed in vessel 16; the vessel was connected to the copper lid and tube 14 by two flanges 15 strengthened with bolts, and the system pumped out through valve 13 with valve 12 closed. The high-temperature hermetization of vessel 16 was achieved by means of the conical clamp indicated in the figure. Visible evolution of DF began during heating of the salt to 450-500° in vacuo; DF passed through condenser 17 and test tube 18 packed tightly with teflon shavings, after which it entered into the receiving flask 19 cooled by a mixture of dry ice and acetone (−78°). To prevent the condensation of deuterium fluoride in test tube 18, it was immersed in a glass containing warm water. Almost complete decomposition of the bifluoride was achieved at 550-600°C. About 600-620 g of DF were obtained from 2.4 kg of the salt.

To purify DF from traces of the salt, the DF was redistilled several times through volumns 9, 40 cm in diameter; these columns were packed tightly with teflon shavings. Distillation was continued until the electric conductivity (at room temperature) reached $3\text{-}4 \cdot 10^{-3} \Omega^{-1}$ cm $^{-1}$. The cell for measuring DF conductivity is shown in Fig 2. Casing 1 and lid 2 were made of monel metal. By means of teflon gaskets 3, two platinum rods 4 with platinum electrods 5, measuring 1 x 2 cm, were introduced into the cell. To maintain constant the cell's volume, the electrodes were fastened by two teflon plates 6.

Deuterium fluoride was kept in vessel 32, supplied with a siphon and valve 11.

Deuterium trifluoride was obtained by thermal decomposition of KBF_4 (in the presence of $BaCl_2$) in vacuo. Decomposition was conducted at 500-600° in the copper vessel 31 (Fig 1), which was equipped with a conical clamp. The obtained boron trifluoride was cooled in condenser 1, traces of HF were removed by passing the gas through tube 30 with KF, after which boron trifluoride was distilled in vacuo several times from trap 29 into trap 27 to remove nonvolatile mixtures. The purified BF_3 was collected and kept in the large flask 3.

All stopcocks and ground ends of the apparatus were lubricated with carbon tetrafluoride vacuum oil, which is resistant to both HF and BF_3.

The central part of the apparatus, shown in Fig 1, is used for dosage and separation of deuterium fluoride. All vessels and test tubes operating with DF, as well as their covers, were cut out from monel metal. In cases when it was impossible to avoid soldering, copper-silver solder was used.

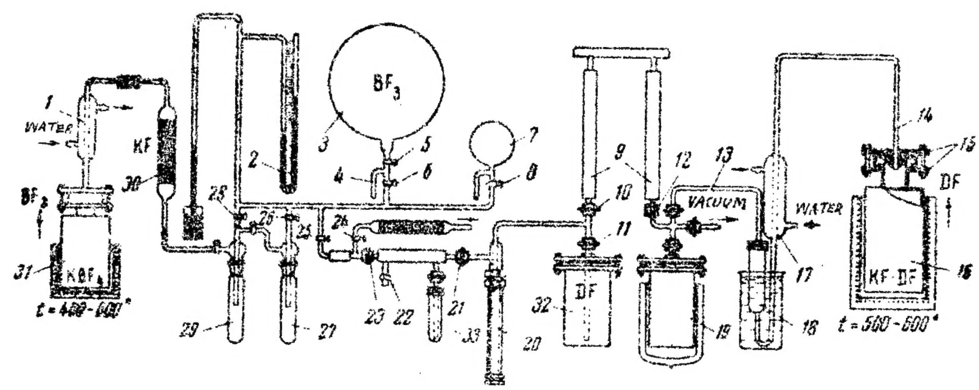

Fig. 1

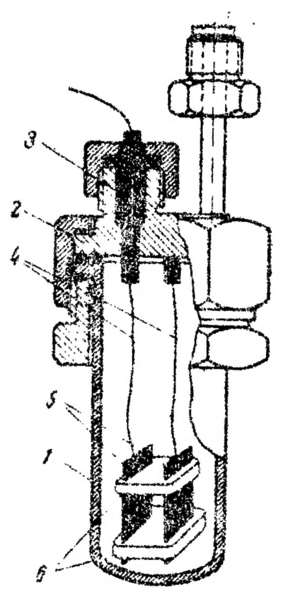

Fig. 2

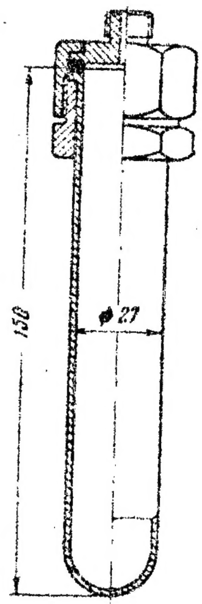

Fig. 3

A test tube containing a valve, which is illustrated separately in Fig 3 [4], was joined to the free connecting pipe 22 with a plasted-on screw. A part of the apparatus was pumped out to valves 10 and 11, valves 21 and 23 were closed, valve 11 was opened slightly and carefully and a determined quantity of DF siphoned off from the receiving flask 32 into the transparent, calibrated test tube 20 prepared from poly (trifluorochloroethylene). After siphoning, valve 11 was closed, valves 10 and 21 were opened and, after the test tube was cooled (Fig 3), all the DF was distilled into it from the calibrated tube 20. When the distillation was completed, valve 21 was closed and the test tube disconnected from connecting pipe 22.

Dosage and separation of HF_3 from flask 3 were accomplished in the following manner: The glass part of the apparatus was pumped out through stopcocks 25 and 24 into stopcock 28 and 26, after which stopcock 25 was closed with stopcock 8 open a known amount of BF_3 from vessel 3 was admitted through valves 5 and 6 into the apparatus. The pressure of BF_3 in the system was measured with manometer 2. After separating the required amount of BF_3, stopcocks 5 and 8 were closed. BF_3 was collected in extension 4, the latter being cooled by liquid air; whereupon, with stopcock 6 closed and stopcock 5 open, BF_3 was evaporated from extension 4 into vessel 3. The amount of BF_3 remaining in calibrated flask 7 may be calculated without difficulty since the flask volume and gas pressure are known. The weighed portion of BF_3 was distilled over from flask 7 through stopcock 25 and valve 23 into the liquid-air cooled test tube joined to connecting pipe 22.

All connections were accomplished by means of connecting pipes equipped with mutually exchangeable nuts of a standard one-quarter inch thread.

The valve construction is illustrated in Fig 4. Frame 1, rod 2 and supporting ring 3 were prepared from monel metal, and gasket 4 -- from teflon. The remaining parts were made from brass and steel. This valve possess a number of advantages of particular value when operating with hydrogen fluoride. In the first place, piston 2 does not revolve but gradually moves upwards and downwards. This is accomplished by introducing an additional thread in the upper part of the piston into which screw 5 is fitted, and also by the presence of crosspiece 6 shifting along the vertical groove in casing 7 of the valve.

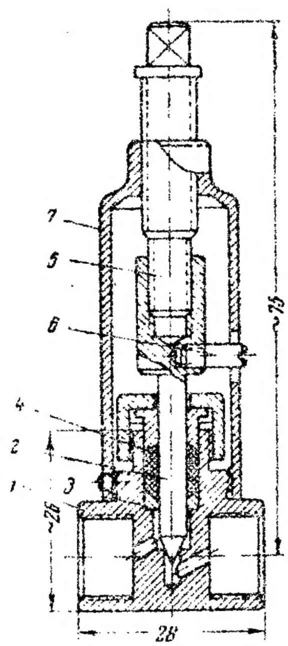

Fig. 4

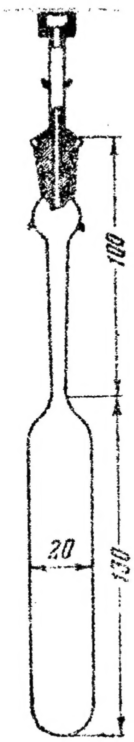

Fig. 5

This assists in better hermetization of the valve and protects the needle and seat from wear. In the second place, opening and closing of the valve may be accomplished by the piston's delicate movement. This is achieved with the help of the two threads on the lower and upper parts of screw 5, each thread having a different pitch. The speed of the piston's delivery is determined by the pitch difference. In the third place, a minimal amount of corrosion-resistant material is used in valve production.

A specific characteristic of the method is that the investigated solutions in liquid HF are contained in opaque metallic vessels. When it was necessary to observe the behavior of the solutions in liquid HF, to ascertain their color or the solubility limits of the investigated substances, the experiments were conducted in transparent quartz ampoules. For this purpose, to the free connecting pipe 22 (Fig 1) there was screwed on a monel-metal connecting pipe ending in a polished edge, to which a quartz ampoule (Fig 5) was connected. The investigated substance was placed in the ampoule, the polished edge lubricated with fluorocarbonate vacuum oil, and the ampoule connected to the apparatus. Subsequently, as described above, the required amounts of HF and BF_3 were condensed into it, and the test tube was then resoldered at the point of intake. In the absence of air and moisture, the quartz ampoules remained transparent for several hours and were not subjected to severe destruction by the action of HF.

Experiments on the isotope exchange were conducted in the following manner: A weighed portion of the substance was introduced into a monel-metal test tube which was then joined to the free connecting pipe 22 (Fig 1), and the required amounts of DF and BF_3 were added (as described above). During the rapid reactions, it is essential to establish with sufficient accuracy the precise moment when the exchange begins at a given temperature. This is difficult to accomplish if the test tube containing the solution had been cooled by liquid air at the start of the experiment. To obtain a more accurate calculation of the beginning of the reaction intermediate test tube 33 (Fig 1), supplied with a siphon, was used during the preparation of the solution. After the test tube had been cooled in a freezing mixture ($--78^o$), DF was distilled into it from the calibrated test tube; it was then heated to the required temperature, and DF was siphoned off into the reaction test tube containing the weighed substance. The test tube was then detached from the apparatus, shaken up to accelerate the solution of the substance, and placed in a thermostat. As was shown by special

experiments, it is possible by this method of solution preparation to fix the time of the start of the exchange-reaction with an accuracy of approximately ±30 seconds. The DF dosage was realized by means of calibrated test tube 20 (Fig 1), and the precise weight was established by weighing the test tube containing the substance, before and after the preparation of the solution in DF. The temperature and duration of the experiment of the exchange were noted.

Separation of small amounts (about 0.3 g) of the organic substances from DT (15 g) at the end of the experiment was accomplished by various methods, depending upon the properties of the substance. With highly volatile substances (benzene, toluene, etc.), the solution was frozen and potassium fluoride was added to it. After DF was transformed into potassium fluoride, the organic substance was distilled in vacuo into a small glass test tube. For the separation of substances which volatilize with difficulty, DF was first distilled in vacuo, and the residue was extracted from the test tube with a suitable solvent. After separation the substance was purified, the physical constants (melting point, boiling point, refractive index) were determined, the substance was burned in a stream of hydrogen, and the water obtained from the combustion was purified and its deuterium content determined by the drop method [5].

The deuterium concentration in liquid DF was determined by conducting an isotope exchange reaction with benzene and by determining the deuterium content in benzene after attaining isotope equilibrium. Benzene was chosen because all the hydrogen atoms in its molecule are equivalent, and the exchange reaction takes place quite rapidly, even at room temperature [1]. To take advantage of this method, it was necessary to know the magnitude of the deuterium distribution coefficient α between C_6H_6 and HF. A direct isotope analysis of several specimens, employed in direct tests for the determination of the magnitude α, was fulfilled with the help of two independent methods -- sodium carbonate and mass-spectroscopy. The first consisted of an isotope analysis of water resulting from the reaction between DF and Na_2CO_3. Since an excess of anhydrous sodium carbonate entered into the reaction, as compared with the stoichiometric quantity, the isotope composition of the resulting water was taken as equal to the isotope composition of H_2O. An analogous method of the deuterium-concentration determination in HCl was used in the work of Klit and Langseth [6]. The other method consisted of the isotope mass-

spectroscopic analysis of gaseous hydrogen, resulting from the decomposition of the weighed portion of the DF by excess metallic potassium. Into the monel-metal test tube a soldered ampoule containing metallic potassium was introduced, and a small amount of DF was condensed in it. By means of a monel-metal hammer, placed beforehand into the test tube, the potassium-containing ampoule was smashed. The hydrogen generated as a result of the reaction between DF and potassium was led into a previously exhausted flask, and individual specimens of the gas were subjected to the isotope analysis by the mass-spectrometer. Attempts to determine the deuterium concentration in DF by its reaction with such substances, as MgO, CuO and K_2CO_3, and a subsequent isotope analysis of the resulting water were unsuccessful.

As a result of the experiment on the exchange reaction, we determined the deuterium concentration in water from the combustion of the substance at the end of the experiment (S_V), as well as the weighed portions of the solvent (R_R) and of the solute (R_V). In addition we also determined the deuterium concentration in the solvent at the beginning of the experiment (S_V^0). Knowing the deuterium concentration coefficient (α) between HF and the substance investigated, it was possible with the aid of corresponding formulae [7] to establish the number of hydrogen atoms entering into the exchange reaction under the experimental conditions.

We express our gratitude to Prof A. I. Shatenshteyn for valuable advices.

Summary

A description is given of a method for obtaining pure liquid hydrogen fluoride enriched with deuterium, and of a procedure for isotopic hydrogen exchange studies in this solvent.

Physico-Chemical Institute
im. L. Ya. Karpov
Moscow

Submitted 29 June 1956

Bibliography

1. Varshavskiy, Ya. M.; Shatonshtoyn, A. I. DAN, 95, 297, 1954.

2. Clausson, W.; Hildobrand, J., Journ. Amor. Chom. Soc., 56, 1,820, 1934.

3. "Inorganic Syntheses"; Vol. I, Symposium edited by Buz. Translated from English by IIL, 1951, page 132.

4. Shatonshtoyn, A. I. Journal of Physical Chomistry, 15, 246, 1941.

5. Shatonshtoyn, A. I.; Varshavskiy, Ya. M.; Dykhno, N. M.; Zvyagintsova, Yo. N.; Izrailevich, Yo. A.; Kalinachonko, V. P.; Yakovlova, Yo. A., Isotopo Analysis of Water, Publishing Houso AS USSR, 1954.

6. Klit, A.; Langsoth, A., Naturo, 135, 956, 1935; Zs. Phys. Chom., A176, 65, 1936.

7. Varshavskiy, Ya. M.; Kalinachonko, B. R., Journal of Physical Chomistry, 30, 1,376, 1956.

END